EFFECTS OF HEAVY RECYCLE SOLVENT COMPONENTS ON DIRECT COAL LIQUEFACTION

James R. Longanbach

Battelle Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

Introduction

The quality of the recycle solvent is critically important in all direct coal liquefaction processes. The fact that overall solvent quality can be greatly improved by adding some of the lighter nondistillable products to the solvent is one of the most important discoveries in direct coal liquefaction research in recent years.[1] Many recent studies have focused on the role of solvent in direct liquefaction. It has been shown that most hydrogen transferred to the dissolving coal during initial preasphaltene formation comes from the solvent rather than hydrogen gas.[1,2] The high molecular weight aromatic hydrocarbons in the recycle solvent are particularly adept at transferring hydrogen to coal and can retard retrogressive reactions which can lead to the formation of undesirable insoluble products. On the other hand, the coke formation reactions are also caused in large part by high molecular weight solvent components, particularly those containing phenolics and polyfunctional compounds.[4]

Other studies have focused on the role of nitrogen-containing aromatics in the recycle solvent. The lower molecular weight aromatics which contain basic nitrogen have been shown to be excellent hydrogen transfer agents[4] and may also readily penetrate the coal structure to react with reactive coal species before retrogressive reactions can take place.[5]

One of the problems encountered in all of these studies has been that when actual process derived solvents are used, they are so complex that the results are hard to assign unambiguously to particular chemical properties of the solvent, while the use of model compounds have simply not included materials of sufficiently high molecular weight to adequately represent the heavier species in true recycle solvents.

The purpose of this work is to further study the liquefaction chemistry of the heavier materials in a process derived liquefaction solvent. Solvents obtained from near equilibrium operation of the Lummus ITSL Process are being used because others have shown that this solvent is less complex than solvents from other processes.[6]

Experimental

Samples of SCT Recycle Solvent (2SCT16-1122), the solvent recycled to the short contact time coal dissolution step, and SCT Heavy Oil Product (2SCT16-1122), the 500^{+}F product from the same process step, were obtained from the Lummus ITSL Process pilot plant.

Both of these materials are black solids at room temperature. Analyses are listed in Table 1. Both have number average molecular weights (by vapor pressure osmometry) between 400-500 grams/mole. The SCT Heavy Oil Product, which is approximately a 1.8:1 mixture of reacted SCT Recycle Solvent and dissolved coal, has an H/C ratio of 0.80, slightly higher than the H/C ratio of the starting Illinois #6 coal and somewhat less than the H/C ratio, 0.95, of the SCT Recycle Solvent.

Illinois #6 coal used in the Lummus ITSL Process was also obtained and analyzed with the results shown in Table 2. The coal has been dried to approximately 4 percent moisture and ground to more than 70 percent -200 mesh for use in the process.

The procedure used for the liquefaction studies consists of mixing solvent and coal in a microautoclave (~18 cc volume) and pressurizing with either hydrogen or helium, containing a small amount of krypton as an internal standard, to 1000 psia (at room temperature). Standard reaction conditions are 800 F for 5 minutes. The autoclave is agitated with a wrist action shaker and heated in a fluidized sand bath. The autoclave is equipped with a thermocouple and recording pressure transducer. A typical pressure and temperature versus time curve is shown in Figure 1. The average heatup time, to 790 F, is 1.9 minutes. After reaction, quenching to 600 F requires ~0.5 minutes. This method gives excellent control of residence time at temperature.

The gases are transferred to storage in a 2-liter evacuated gas bulb for later analyses. The liquefaction products are washed from the autoclave with THF and the insolubles are extracted with THF in a Soxhlet extractor. Conversions of MAF THF insolubles are calculated using the weights of insoluble organic material (IOM) in the coal and solvent, the starting ash content of the solvent and coal and the moisture content of the coal. Excess THF is stripped from the THF solubles on a rotary evaporator and the resulting concentrated solution is slowly added to 20 parts of boiling heptane per part of THF to precipitate heptane insolubles. After the THF is distilled from the mixture, the precipitate is allowed to settle overnight and removed by vacuum filtration. The heptane is distilled from the filtrate and each of the fractions is dried in a vacuum oven overnight at 110 C, cooled and weighed. Net changes in the amounts of THF soluble-heptane insolubles (asphaltenes and preasphaltenes) and heptane solubles (oils) are calculated by subtracting blank extraction data for the starting solvent and coal to obtain differential solubility changes caused by liquefaction.

The gases are analyzed for H_2, CO, CO_2, CH_4, C_2's and Kr. After normalization to a standard krypton concentration, net yields (or losses of hydrogen) for each gas are calculated.

Results and Discussion

In order to study the chemistry of the 800$^+$F Recycle Solvent components, the SCT Recycle Solvent was separated by vacuum distillation into fractions with boiling points above and below 800 F (427 C). Liquefaction experiments using the 800$^-$F material serve as a baseline to allow a systematic study of the effects of addition of various fractions of the 800$^+$F materials to the liquefaction solvent. Additional chemical insight may be obtained by running reactions in the presence and absence of a 1000 psia (cold) hydrogen atmosphere. Also, the use of the same chemical class fractions obtained from the 800$^-$F and 800$^+$F fractions may help illustrate the effects of higher molecular weight on the reactions of the solvent.

The SCT Recycle Solvent sample has been distilled under vacuum to obtain 800$^+$F and 800$^-$F fractions with the results listed in Table 3. Approximately 36 percent of the sample distilled below 800 F. The 800$^-$F material has a higher H/C ratio and about 50 percent lower number average molecular weight. As expected, it is almost entirely heptane soluble. The 800$^+$F fraction contains 80 percent of the nitrogen, 84 percent of the sulfur and 76 percent of the oxygen in 65 weight percent of the sample. The heteroatom concentrations are not large, however, and total only about one heteroatom per molecule (containing an average of 34 carbon atoms).

Liquefaction experiments have been done using 6 g of either the total SCT Recycle Solvent or the 800$^-$F SCT Recycle Solvent fraction with 3 g of Illinois #6 coal under 1000 psia (room temperature) hydrogen or helium. The results are listed in Table 4.

Since both solvents and the coal are partially soluble in THF and heptane when exposed to the workup procedure before liquefaction at elevated temperature, the results have been corrected using blank extractions of the starting materials

to reflect the changes in the three solubility fractions before and after liquefaction. The results have also been corrected to remove the ash and moisture present in the starting coal. The reaction conditions have been chosen to obtain good, but not complete conversions so that differences due to the solvent and gas atmosphere can be seen. The reaction conditions gave nearly equal conversions of MAF THF insolubles, except for the 800$^-$F SCT Recycle Solvent under hydrogen, which gave a significantly higher conversion. Most of the THF insoluble material is converted to THF soluble-heptane insolubles (preasphaltenes plus asphaltenes). Under helium there is a small net loss of heptane solubles (oils).

Hydrogen is produced on balance under a helium atmosphere while hydrogen is incorporated into the products on balance under a hydrogen atmosphere. The 800$^-$F SCT Recycle Solvent may be exceptional in this respect and actually release a small amount of hydrogen, even in the presence of 1000 psig of hydrogen. The effects of different solvents and gas atmospheres on CO is negligible but more CO_2 is produced under helium and more CH_4 is produced under hydrogen.

The 800$^-$F and 800$^+$F SCT Recycle Solvent fractions are now being separated into chemical classes using the liquid chromatography method described by Later, et al.[8] Preliminary results from the separation of the 800$^+$F SCT Recycle Solvent fraction are listed in Table 5.

Table 5. Separation of 800$^+$F SCT Recycle Solvent Fraction by Liquid Chromatography

Solvent	Chemical Class	Recovery, Weight Percent
Hexane	Aliphatic hydrocarbons	4.9
Benzene	Aromatic hydrocarbons	27.9
Chloroform	N-Aromatics	4.8
THF-EtOH (10%)	OH-Aromatics	33.3
Total recovery		70.8

The 800$^+$F material is approximately one-quarter aromatic hydrocarbons and 5 percent of aliphatic hydrocarbons and N-aromatics.

These separations will be extended to the 800$^-$F SCT Recycle Solvent fraction and then these fractions will be added separately to the 800$^-$F recycle solvent to determine the effect of various types of solvent molecules on the conversion and yields during the coal dissolution step.

Acknowledgement

The author gratefully acknowledges the receipt of samples from Harvey Schindler and James Chen of Lummus. Bruce Utz, DOE (PETC), provided all of the information needed to construct the microautoclave reactor system. Eneo Moroni, DOE (Germantown) has provided many useful insights to this work. Sayeed Akhtar, DOE (PETC) is the project monitor. This work was prepared with the support of the U.S. Department of Energy, Grant No. DE-FG22-82PC50783. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the author and do not necessarily reflect the views of DOE.

Literature Cited

(1) Process Development for Improved SRC Options; Kerr-McGee Critical Solvent Deashing and Fractionation Studies. Final Report on EPRI Project 1134-2 by Kerr-McGee Corporation, July 1981.

(2) Neuworth, M.B. and Moroni, E.C., "Development of a Two-Stage Liquefaction Process", Adv. Coal Utilization Technology Symposium Papers, 345-58, IGT (1979).

(3) Thomas, M.G., Sample, D.G., and Floyd, J.L., Selectivity of Catalysts Towards Coal-Derived Products, NTIS Sand 79-182GC.
(4) Fundamental Studies in the Conversion of Coals to Fuels of Increased Hydrogen Content, Final Report on EPRI Project 1655-1 by Mobil Research and Development Corporation, November 1981.
(5) The Effect of Basic-Nitrogen Solvents on Coal Conversion, Proceedings of the Seventh Annual EPRI Contractors' Conference on Coal Liquefaction, May 12-14, 1982.
(6) "Advanced Coal Liquefaction", EPRI Journal, P. 31-34, May 1982.
(7) Wilson, B.W., Pelroy, R.A., Mahlum, D.D. and Frazier, M.E., Mutagenicity and Carcinogenicity Test Results on ITSL Process Streams, Proceedings ITSL Program Contractors' Project Review Conference, October 6-7, 1982.
(8) Later, D.W., Lee, M.L., Bartle, K.D., Kong, R.C. and Vassiloros, D.L., Chemical Class Separation and Characterization of Organic Compounds in Synthetic Fuels, Anal. Chem. 1981, 1612-20.

TABLE 1. ANALYSES OF SCT RECYCLE SOLVENT AND HEAVY OIL PRODUCT FROM THE LUMMUS ITSL PROCESS PILOT PLANT

Sample	SCT Recycle Solvent (2SCT16-1122)	SCT Heavy Oil Product (2SCT-1122)
Elemental Analyses, Wt %		
Ash	1.30	3.61
Carbon	86.77	85.87
Hydrogen	6.88	5.74
Nitrogen	0.94	1.02
Sulfur	0.53	0.99
Oxygen (by difference)	3.6	2.8
H/C	0.95	0.80
Distillation Data, Wt %		
800⁻F	35.6	38.2
800⁺F	64.4	61.8
THF Solubility, Wt %	96.4	88.6
Molecular Weight, g/mole	477	424

TABLE 2. ANALYSES OF ILLINOIS #6 COAL FROM THE LUMMUS ITSL PROCESS PILOT PLANT

Proximate Analyses, Wt %	As-Received	Dry
Moisture	3.99	-
Ash	9.72	10.12
Elemental Analyses, Wt %		
Carbon	69.73	72.63
Hydrogen	4.93	4.67
Nitrogen	1.18	1.23
Sulfur	2.88	3.00
Oxygen (by difference)		8.35
H/C		0.77
Particle Size Distribution, Wt %		
+70 mesh	0.07	
-70 +120	3.64	
-120 +200	18.90	
-200 +325	14.84	
-325	62.55	
THF Solubility, Wt %	13.7	

TABLE 3. ANALYSES OF 800⁻F AND 800⁺F FRACTIONS FROM THE DISTILLATION OF SCT RECYCLE SOLVENT (2SCT16-1122)

Sample	800⁻F	800⁺F
Weight % of Starting Material	35.6	64.4
Elemental Analyses, Wt %		
Carbon	90.96	87.88
Hydrogen	7.12	6.18
Nitrogen	0.57	1.30
Sulfur	0.23	0.69
Oxygen (by difference)	1.12	1.95
Ash	<0.01	2.00
H/C	0.94	0.84
Molecular Weight, g/mole	257	456
Solubilities, Wt %		
THF insolubles	0.0	5.5
Heptane insolubles	1.5	39.5
Heptane solubles	98.5	57.9

TABLE 4. SUMMARY OF MICROAUTOCLAVE LIQUEFACTION RESULTS WITH SCT RECYCLE SOLVENTS AND ILLINOIS #6 COAL

Run No.	7	15	9	17
Solvent	Total SCT Recycle Solvent		800⁻F SCT Recycle Solvent	
Gas Atmosphere	He	H_2	He	H_2
Conversion of MAF THF Insolubles, %	78.2	75.0	78.6	84.6
Net Change of Heptane Insolubles, % of Total MAF Products	19.0	17.8	18.0	19.2
Net Change of Heptane Solubles, % of Total MAF Products	-2.0	0.5	-0.0	1.1
Gas Analyses, Volume %				
H_2	0.85	-7.87	1.09	1.55
CO	0.16	0.12	0.13	0.14
CO_2	1.06	0.75	1.15	0.58
CH_4	0.77	0.98	0.75	0.90
C_2H_4/C_2H_6	0.49	0.39	0.35	0.34

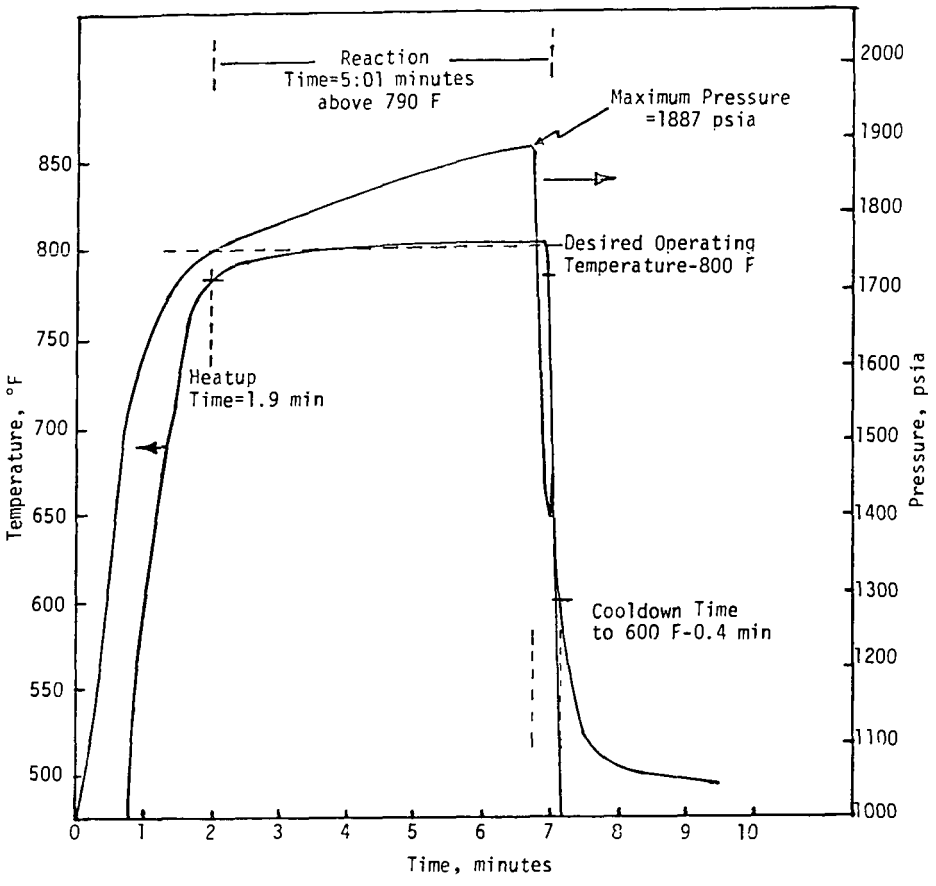

FIGURE 1. TYPICAL MICROAUTOCLAVE PRESSURE, TEMPERATURE VERSUS TIME CURVE FOR SRT COAL LIQUEFACTION